

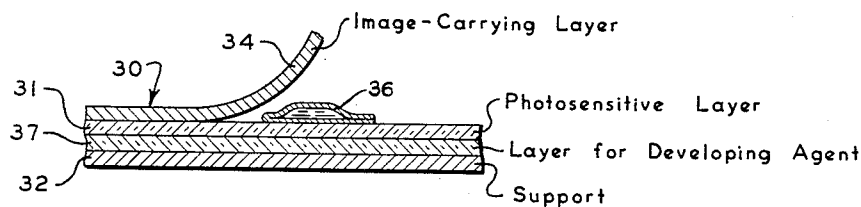
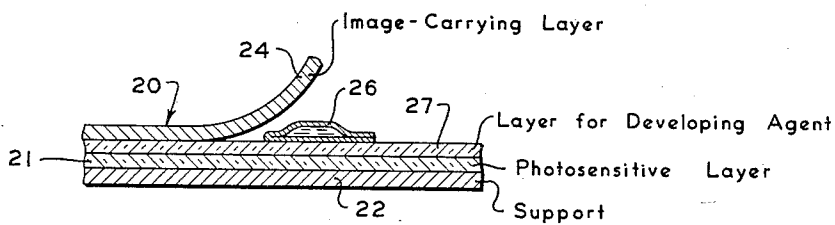
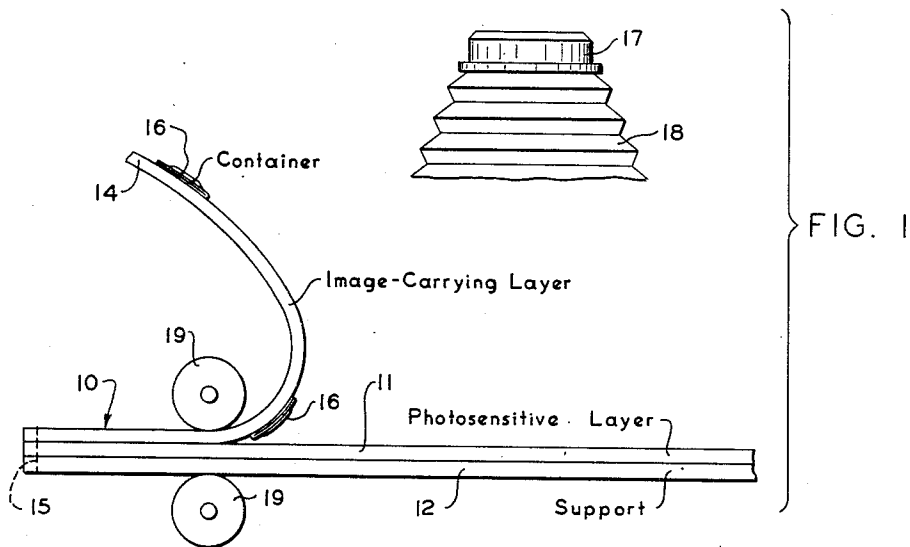
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E. H. LAND

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PHOTOGRAPHIC PRODUCT AND PROCESS

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PHOTOGRAPHIC PRODUCT AND PROCESS

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This invention relates to the art of photography and more particularly to novel processes for the formation of dye images and to film units for use with such processes.

This application is a continuation-in-part of my copending application Serial No. 702,039, filed October 8, 1946, for Photographic Product and Process.

An object of the present invention is to provide an improved process for forming a dye positive image of a negative latent image contained in a photosensitive silver halide emulsion layer of a photographic element and particularly to an improvement of such process whereby the formation of a solution of materials potentially capable of entering into a dye-forming reaction is caused to occur within said photographic element and wherein an imagewise distribution of said materials capable of entering into a dye-forming reaction is transported in solution from the photographic element to a permeable image-carrying layer and are there reacted to provide a dye positive image in said image-carrying layer.

Other objects of the invention are to provide a process for forming, in a permeable image-carrying layer of a film unit, a dye positive image of a latent negative image contained in a photosensitive silver halide emulsion layer of a negative sheet material adapted to be arranged in superposed relationship with said image-carrying layer by practices which develop said latent image to silver and form a dye in said negative sheet material while also forming in said sheet material a solution of materials potentially capable of entering into a dye-forming reaction, and wherein an imagewise distribution of said materials capable of entering into a dye-forming reaction is transferred in said solution to said image-carrying layer where said potential dye-forming materials are converted to a dye positive image by causing said dye-forming reaction to occur; to provide a process of the character described wherein a liquid composition is spread between the image-carrying layer and the negative sheet material of a film unit in a condition incapable of creating a dye in said image-carrying layer but which upon permeation into the negative sheet material is modified by formation into a solution of materials which are capable of entering into a dye-forming reaction; as well as to provide a process of the character described wherein the liquid composition spread between the image-carrying layer and the negative sheet material of a film unit contains a mutual solvent for color-former material and a developing agent capable of developing exposed

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silver halide to silver and also capable when in oxidized condition of coupling with said color-former material to provide dye, the color-former material and the developing agent both entering into solution with said solvent only after it has permeated into the negative material, and wherein said solvent is utilized to transport an imagewise distribution of unreacted color-former material and unreacted developing agent to said image-carrying layer for oxidation of the unreacted developing agent to effect a coupling reaction to provide the desired dye positive image.

Further objects of the invention are to provide novel film units which permit the practice of the processes herein described and which make use of a photographic element such as negative sheet material having at least a silver halide emulsion layer, a permeable layer constituting an image-carrying layer adapted to be brought into superposed relationship with the photosensitive layer, a fracturable container for a liquid-processing composition carried by a layer of said film unit and a processing composition comprising a mutual solvent for materials potentially capable of entering into a dye-forming reaction and including color-former material and a developing agent characterized by its ability to develop exposed silver halide to silver and when oxidized to couple with color-former material to provide dye; and to provide film units of the character described which are constructed and arranged to permit either or both said color-former material and said developing agent to be incorporated within some layer of the negative sheet material, and particularly within the photosensitive layer thereof, or to permit the developing agent or the color-former material to be included in the container in the liquid composition carried therein, and also to permit a weak oxidizing agent to be distributed within the image-carrying layer.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and the relation of components and the processes involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in

connection with the accompanying drawing wherein:

Figure 1 is a diagrammatic view of one embodiment of film unit forming the subject of this invention and also diagrammatically illustrates one manner in which such film unit may be exposed and processed in a camera apparatus shown in conjunction therewith;

Fig. 2 is a diagrammatic cross-sectional view of another embodiment of film unit; and

Fig. 3 is a diagrammatic cross-sectional view of still another embodiment of film unit.

In general, the photographic processes and products disclosed herein are concerned with the treatment of a latent negative image in a photosensitive silver halide layer whereby to provide a stable dye positive image thereof in or on another layer hereinafter referred to as an image-carrying or image-receiving layer.

Application Serial No. 702,039, filed October 8, 1946, by Edwin H. Land for Photographic Product and Process has disclosed one such practice wherein a photographic negative material such as a photographic element or sheet material comprising at least a silver halide emulsion layer having a latent image therein is processed to form in a permeable image-carrying layer a dye positive image of the latent image by bringing such an image-carrying layer into superposed relationship with the photosensitive layer and by spreading between and permeating into such layers a liquid-processing composition which comprises an alkaline aqueous solution of a color former and a secondary color-forming developing agent.

Under these conditions the solution of the developing agent and coupler permeates the photosensitive layer where the developing agent reduces the exposed silver halide of the latent image to metallic silver and the portions of the developing agent which are oxidized as a result of silver development react with the coupler in the solution and form a dye image which is co-extensive with the silver image. The unreacted developing agent and coupler in the remaining solution provide positive image-forming components which migrate or diffuse from the photosensitive layer to the image-carrying layer and form thereon an imagewise distribution of unreacted developing agent and unreacted coupler which upon oxidation of the unreacted developing agent effect formation of the desired dye positive image in the image-carrying layer. Oxidation of the unreacted developing agent to cause the desired coupling reaction may be effected by an oxidizing agent incorporated in the image-carrying layer or the coupling may be carried out by aerial oxidation of the developing agent after formation in the image-carrying layer of the imagewise distribution of the unreacted developing agent and unreacted color former.

The present invention is concerned with improvement of the just-described processing and the products used to carry these practices into effect whereby to improve positive image rendition and pictorial quality. In accomplishing these desiderata, utilization is made of a liquid composition which at the time it is spread between the image-carrying layer and photosensitive layer is incapable of creating a dye on or in the image-carrying layer and by modifying the spread liquid after it has permeated into the negative sheet material to place it in a condition capable of forming a dye upon the carrying out of an oxidation reaction. Consequently, the

liquid composition when spread will contain only one or none of the materials which are potentially capable of entering into a dye-forming reaction or, to put it another way, either or both of said materials, i. e., the color former or coupler and the secondary color-forming developing agent are incorporated in some layer of the sheet material or photographic element of which the photosensitive layer is a part.

In all embodiments of the invention, dye is preferably created by a coupling reaction between a coupler or color former and a secondary color-forming development agent, i. e., a developing agent which when oxidized will react with a coupler to create a dye. A preferred modification of the invention incorporates the coupler or color former in the photosensitive layer and dissolves the developing agent in the liquid composition to be spread between the layers while incorporating an oxidizing agent in the image-carrying layer.

In another modification of the invention, which utilizes an oxidizing agent in the image-carrying layer, both the color former and the developing agent are incorporated in the photosensitive layer. A further modification utilizes an image-carrying layer having an oxidizing agent therein and in conjunction therewith a sheet material comprising a photosensitive layer and at least one other permeable layer whereby the coupler may be placed in either permeable layer and the developing agent in the other such layer or whereby both the coupler and the developing agent may be placed in some permeable layer other than the photosensitive layer.

The invention is not limited to use with a single coupler in a photosensitive layer but in a further modification comprehends the incorporation in a photosensitive layer of several different color formers whereby to give a positive image having a color different from each of the individual dyes formed upon coupling of the different color formers.

Color formers employed in the practice of the invention should be at least partially soluble and mobile in an alkaline aqueous solution, such as the liquid-processing compositions hereinafter described. On the other hand, dyes resulting from the coupling of such color formers with a developing agent should be relatively insoluble or immobile in alkaline solution whereby dye formed in the sheet material which carries the photosensitive layer remains therein and its diffusion into the image-carrying layer is substantially prevented. At the same time, the color formers employed should preferably have such solubility in alkaline solution that they do not dissolve therein to an extent whereby they migrate from the photographic negative material prior to initiation of the development reaction so that the color-former material will remain in the neighborhood of the developing silver halide grains whereby to guarantee coupling in the negative material wherever silver development takes place.

The couplers or color formers are preferably of a character such that they form azomethine, indaniline and indophenol dyes when reacted with a secondary color-forming developing agent which has been oxidized. Such color formers may comprise nitriles, acyl nitriles, thioindoxyls, cyanacetanilides, pyrazolones, phenols, naphthols, substituted ketones, esters and acyl acetanilides. As examples of a few of the many color formers which may be used with the invention, specific

mention may be made to those in the following list:

p-Nitrophenylacetonitrile
Cyanacetophenone
p-Nitrobenzoylacetonitrile
Bromothioindoxyl
Cyanaceto-B-naphthalide
1-Cyanacetaminobenzothiazole
1-Phenyl-3-furyl-5-pyrazolone
1-Phenyl-3-methyl-5-pyrazolone
Pentachlorophenol
o-Hydroxydiphenyl
2,4-dichloro-6-cyclohexylphenol
Hydroquinone monobenzyl ether
2,4-dichloro-1-naphthol
Pentabromonaphthol
5,7-dibromo-8-hydroxyquinoline
Benzoyl acetone
B-naphthoyl acetone
Benzoyl acetic ester
Acetoacetanilide
Acetoacet-2-chloroanilide
1-chloroacetoacetanilide
Ethylacetoacetate

Developing agents for use with these color formers comprise such secondary developing agents as the p-phenylenediamines, the aminophenols and their alkyl substituted derivatives, and others characterized by their ability when oxidized to condense with couplers to form dyes of the above type. Combinations of developing agents and color formers which form the least soluble and/or least mobile dyes are preferred since such combinations gives the clearest highlights and the sharpest detail to the positive image.

A wide variety of oxidizing agents, adapted to be incorporated in the image-carrying layer by imbibition, are suitable for use in putting the invention into practice although their selection will be dependent upon their ability to oxidize the developing agent without substantially affecting the dye formed as a result of the color-forming reaction between the oxidized developing agent and the coupler. Oxidizing agents which are of such powerful and strong nature that they seriously impair a dye of the character utilized by this invention by bleaching or otherwise attacking the dye are obviously unsuitable. As indicative of what is meant by powerful oxidizing agents reference is made to substances such as bromine, iodine, hydrochloric acid, chromic acid, nitric acid and the like.

As examples of oxidizing agents of a sufficiently weak character to be useful with this invention mention may be made of peroxy compounds such as sodium or potassium perborate, sodium or potassium perchlorate, sodium or potassium peroxide, sodium or potassium permanganate, barium or zinc or cadmium peroxide and ammonium persulfate. Certain dichromates, for example, ammonium dichromate, are also useful for oxidizing agents. Particularly useful oxidizing agents may be found in the readily reducible compounds and especially the salts of the polyvalent heavy metals, i. e., compounds wherein the polyvalent metallic elements is in higher valent form. Examples thereof may be found in compounds of copper, antimony, uranium, manganese and iron wherein the metallic element is in higher valent form.

The compounds having polyvalent metallic elements in higher valent form are reduced by the unreacted developing agent which, as a result, becomes oxidized. At the same time, these salts of polyvalent metals appear to display an affinity for either or both materials entering into the dye-forming reaction or for the resulting dye and in this respect seem to act as a mordant. Whatever may be the action of these reducible compounds of polyvalent metals, the fact is that

image density is increased over that obtained under a similar set of conditions but with the employment of other oxidizing agents.

The preferred polyvalent metallic compounds are cupric salts and as specific examples thereof cupric sulfate, chloride, acetate and stearate are noted. Of these examples of cupric salts, cupric sulfate is preferred. Cupric sulfate and potassium thiocyanate provide a highly useful oxidizing agent when the image-carrying layer is successively imbibed therein and is then washed. In the latter instance, it is believed that the resulting paper contains some cupric hydroxide and some copper thiocyanate.

In addition, aerial oxidation may be utilized for the purpose of oxidizing unreacted developing agent in or on the image-carrying layer to effect positive image formation. When such practice is followed, it is desirable to use a material for the image-carrying layer which contains a dye mordant. Material of this nature is found in conventional dye-transfer papers and for this purpose good results have been obtained by using dye-transfer paper such as that sold by Eastman Kodak Company under the name "Dye Transfer Double Weight F." As other examples of image-receiving layers having a mordant, mention may be made of gelatin in which nickelous sulfate or aluminum sulfate has been uniformly distributed.

The liquid-processing composition employed in carrying out the invention comprises at least an aqueous alkaline solution of sufficient alkalinity to permit the developing agent to perform its developing function and in certain instances may also have the color-former material or the developing agent dissolved therein. A viscosity-increasing compound constituting a film-forming material of the type which, when spread over a water-absorbent base, will form a relatively firm, dimensionally stable film, is preferably included in the liquid-processing composition to assist in spreading the composition in a uniform film between the layers of the film units hereinafter described. A preferred film-forming material is a high molecular weight polymer as, for example, a polymeric, water-soluble ether inert to an alkali solution such as hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents may be employed when their ability to increase viscosity is substantially unaffected when left in solution for long periods of time. The film-forming material is preferably contained in the processing composition in suitable quantities to impart to the composition a viscosity in excess of 1,000 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 200,000 centipoises at said temperature.

One embodiment of a film unit suitable for carrying out the invention is shown diagrammatically and in exaggerated enlargement at 10 in Fig. 1 wherein the unit is schematically illustrated as undergoing exposure in camera apparatus which has mechanism for processing the film unit after the exposure thereof whereby to effect the desired positive image formation and which embodies the principles of the camera apparatus forming the subject of Patent No. 2,435,717, issued February 10, 1948, to Edwin H. Land for Developing Camera Utilizing a Film, Another Sheet Material, and a Fluid Processing Agent.

Film unit 10 of Fig. 1 employs a photographic element such as sheet material comprising any negative film or paper of conventional construc-

tion having a silver halide emulsion or photosensitive layer 11 supported on a support or base 12. Coupler or color-forming material is adapted to be incorporated in the photosensitive layer 11. An image carrying layer 14 of permeable material is associated with the photosensitive layer of the unit 10, and may be carried on a support or base as in the case of imbibition or dye-transfer papers and the like. In the preferred practice of the invention, the image-carrying layer of each film unit has an oxidizing agent incorporated therein.

In the film unit 10, a fracturable container 16 adapted to carry the liquid-processing composition is positioned transversely of and adhered to the image-carrying layer 14 adjacent each image area thereof. Consequently, each container 16 will be located adjacent to a corresponding image area on the photosensitive layer 11 when the image-carrying layer and the photosensitive layer are in contact. Each container 16 is of a length approximating the width of the film unit and is constructed to carry sufficient liquid composition to effect negative image formation in an exposed image area of the photosensitive layer and positive image formation in the corresponding image area of the image-carrying layer 14.

A container 16 may be formed from composite sheet material comprising an inner layer which is substantially chemically inert to the liquid composition used for processing the film unit, an intermediate layer which is substantially impervious to vapor, and an outer or backing layer which can be readily adhered to some layer of the film unit. Materials for the inner layer of the container 16 may be found among the polyvinyl acetals of which polyvinyl butyral and polyvinyl acetal itself are examples while the intermediate layer may comprise metal foil such as lead or silver foil and the outer layer may comprise a suitable paper such as kraft paper. A container may be formed by folding such a composite sheet upon itself, adhering the free edges of the folded sheet together at one end and on a side thereof and, after filling the container, sealing the open end thereof by adhering the free edges together. A detailed description of containers of this type and methods for producing the same is found in application Serial No. 652,612, filed March 7, 1946, by Edwin H. Land for Fluid Containers.

As will subsequently become apparent, other layers of the film unit may be employed in place of the image-carrying layer as a support for the one or more containers used with the unit.

In all types of film units employed in the practice of the invention, it is preferable to expose the negative material from the emulsion side thereof to prevent geometrical reversal of the positive image and to maintain good definition. It is therefore desirable to arrange the image-carrying layer in superposed relationship with the photosensitive layer and to connect one end of the image-carrying layer to the negative sheet material whereby to permit the image-carrying layer to be spread apart from the photosensitive layer in a manner similar to that disclosed in Fig. 1 so that the photosensitive layer may be exposed from the emulsion side thereof and so that the image-carrying layer may be brought into intimate contact with the photosensitive layer after exposure has occurred. The negative sheet material and the image-carrying layer may be connected by fastening means 15 such as those

disclosed in Fig. 1 and comprising one or more hinges, staples or the like.

When the film unit 10 is of the roll film type, the photographic element 11—12 and the image-carrying layer 14 are wound into separate rolls and the free end of each roll is connected together in the manner already described. Such an expedient permits the film unit 10 to be employed with camera apparatus provided with an objective lens and shutter and diaphragm mechanism which are indicated at 17 in Fig. 1 and which are connected by bellows 18 to the light box or exposure chamber of a housing (not shown) within which latter the rolled negative material 11—12 and the rolled image-carrying layer 14 are rotatably and removably mounted.

With reference to Fig. 1 it may be observed that the photographic element 11—12 may be moved through the exposure chamber of the apparatus with the emulsion side thereof facing the objective lens and may be maintained in separated condition from the image-carrying layer 14 during its movement through the exposure chamber by mounting the rolled photographic element and the rolled image-carrying layer on opposite sides of the bellows 18 and threading their joined ends through pressure rollers 19 carried within the camera housing on the same side of the bellows as the mounting for the image-carrying layer. Rolls 19 are pressed together and perform the several functions of moving or at least assisting in moving the film unit 10 through the camera as well as serving to bring the image-carrying and photosensitive layers into intimate contact and in addition fracture the containers 16 in their passage therebetween by the application of mechanical stress thereto and effectively spread the liquid composition between the contacted layers.

Operation of the camera apparatus will now become apparent. Rollers 19 are rotated after an exposure has been made to move the exposed portion of the negative-forming material 11—12 therebetween. At the same time, a portion of the image-carrying layer 14 equal in length to the exposed portion of the photosensitive layer 11 is moved into contact with such exposed portion and a container 16 is fractured to initiate image formation in the portions of the photosensitive and image-carrying layers which have been brought into contact while simultaneously with such operations raw stock necessary for the next exposure is advanced into operating position. The exposed and processed portion of the film unit 10 may be removed from the camera apparatus through a suitable opening in the housing thereof without subjecting the film supply remaining in the camera to actinic light.

As already mentioned, the photosensitive layer 11 of the film unit 10 has a coupler or color former incorporated therein and the image-carrying layer contains an oxidizing agent of the character already set forth. Under such circumstances, each container 16 will carry a developing agent. However, the film unit 10 without change in structure and by incorporating the developing agent in one of the layers of the element 11—12 is capable of several variations so that it may be named as the preferred type of film unit.

For example, the developing agent may be incorporated in the photosensitive layer itself. This may be accomplished by mixing the developing agent and the coupler with the emulsion before the emulsion is cast on the support 12 or, as it will appear in the examples which follow,

the developing agent may be imbibed into the photosensitive layer. Under such circumstances, the developing agent will be omitted from the liquid-processing composition carried within the container 16. In a further variation, the developing agent may be incorporated in the support 12 when the support is a suitable hydrophilic material such as paper or the like by imbibition of a solution formed by dissolving the developing agent in an organic solvent which will not permeate gelatin of the photosensitive layer.

Another embodiment of film unit, indicated by the reference numeral 20, is disclosed in Fig. 2 as comprising a conventional support 22 which carries a photosensitive silver halide layer 21 in which a coupler or color former is incorporated and which, in turn, has a layer 27 of hydrophilic material such as gelatin, polyvinyl alcohol, regenerated cellulose or the like, coated thereon. Layer 27 has the developing agent incorporated therein and one or more containers 26 are carried on the layer 27. An image-carrying layer 24, similar to the layer 14 of Fig. 1, is employed with the unit 20 of Fig. 2.

Still another embodiment of film unit is disclosed in Fig. 3 at 30 and is similar to the unit of Fig. 2 with the exception that the layer 37 thereof which is adapted to have the developing agent incorporated therein, is located between the support and the photosensitive layer 31. Other elements of the film unit 30 comprise one or more containers 36 and the image-carrying layer 34 similar to the image-carrying layers 14 and 24 of the previously described film units. As in the case of the containers 26, the developing agent is omitted from the liquid composition carried therein.

The image-carrying layer is preferably gelatin which is generally carried on a support, an example thereof being found in imbibition paper. Other excellent image-carrying materials comprise papers such as those known in the art as baryta paper and dye-transfer paper. In fact any material dyeable from alkaline solutions may be employed as an image-carrying layer, such materials including water-permeable plastics, or water-permeable, reversible, film-forming organic colloids capable of having high viscosity characteristics and appreciable jelly strength. Specific examples of other dyeable layers are regenerated cellulose; polyhydroxy alkanes, such as polyvinyl alcohol; sodium alginate; cellulose ethers, such as methyl cellulose, or other derivatives, such as sodium carboxymethyl cellulose or hydroxyethyl cellulose; papers; proteins, such as glue; carbohydrates, such as gums and starch; and mixtures of such materials where they are compatible. When the above materials are transparent they may, if desired, be mounted on an opaque base, or, a colloidal pigment may be incorporated in such material to render the same opaque.

Base materials when employed to support an image-carrying layer may be any material of the character used as a base for conventional photographic film and papers. The materials mentioned as suitable for use as image-carrying layers may also be employed in conjunction with a photosensitive layer when the negative sheet material is constructed to have a separate layer in which the developing agent or coupler is incorporated and for this purpose gelatin is preferred. Likewise these materials may be employed as carriers for a silver halide emulsion although as indicated, gelatin is preferred for this purpose and

substantially any commercial negative film or paper may be employed.

To thoroughly instruct the art in the practice of the invention, the following nonlimiting examples are set forth with reference to film units heretofore disclosed by way of giving details as to the materials employed in the construction and processing as well as particulars to techniques employed in color image formation.

Example 1

A negative sheet material or element 11—12 for a film unit 10 of the character illustrated in Fig. 1 is provided by a commercially available film comprising a silver chlorobromide emulsion on a conventional support, such as that sold by Eastman Kodak Company under the name of "Contrast Process Ortho" film. A color former or coupler is incorporated in the photosensitive layer 11 by treatment wherein the sheet 11—12 is immersed for one minute in a bath containing .1 gram of p-nitrophenylacetonitrile per 100 cc. of a solution comprising 20 cc. of acetone and 80 cc. of water. Excess solution is wiped off the element 11—12 as by squeegeeing and the element is dried in air and rinsed for 2 seconds in a solution comprising 90% of acetone and 10% of water and is again squeegeed and dried after which it is ready for use.

An image-carrying layer 14 to be employed with the just-described photosensitive layer is a sheet of baryta paper having a weak oxidizing agent uniformly distributed at least throughout a surface portion thereof. The baryta sheet is prepared with the oxidizing agent by swabbing with a 1% aqueous solution of sodium perborate and is dried.

The liquid composition for each container 16 in this specific embodiment comprises a predetermined quantity of a viscous alkaline aqueous solution of a secondary color-forming developing agent and may be prepared by thoroughly mixing the following materials:

40 grams of a 14% solution of sodium carboxymethyl cellulose in water
5 grams of sodium carbonate
.9 gram 2-amino-5-diethylaminotoluene monohydrochloride
33 cc. of water

In the use of the just-described embodiment of the invention, the photosensitive layer 11 may be exposed in camera apparatus of the character disclosed and the composite product is drawn between the pressure rollers 13. As the container 16 passes through these rollers, its contained liquid is released and spread in a uniform thin layer between the photosensitive layer 11 and the image-carrying layer 14. When a layer of the just-noted liquid-processing composition is spread between the exposed photosensitive layer and the image-carrying layer following fracture of the container, the liquid migrates into the photosensitive layer where the developing agent commences to develop the exposed silver halide grains. At the same time, the alkaline liquid starts to dissolve the color former in the photosensitive layer.

Where the developing agent reacts with exposed silver halide, it is oxidized as a function of the amount of silver halide reduced to silver and the developing agent thus oxidized couples with color-former material adjacent the developing silver grains to form a relatively immobile dye in the negative sheet material 11—12. In all

modifications of the invention, the spread layer of liquid-processing composition is preferably adjusted so that developing agent present in a unit area thereof is in a quantity just sufficient to be completely oxidized by a fully developable or completely exposed portion of the photosensitive layer. Likewise in all modifications of the invention, color-former material available in the photosensitive layer in a unit area of the same magnitude as the previously mentioned unit area is preferably of a quantity just sufficient to be entirely coupled by that amount of developer which is oxidized by the development of a completely exposed unit area of the photosensitive layer.

Consequently, the color-former material is substantially exhausted by coupling with the oxidized developing agent in the area of the highlights of the negative image and is trapped in the sheet 11-12. In places in the negative material where unexposed silver halide grains are present or in places where exposure and consequent development is less than complete, unoxidized developing agent and unreacted color-former material are in solution in proportion to silver development and migrate to the image-carrying layer in an imagewise distribution where the unreacted developing agent is oxidized by the oxidizing agent in the image-carrying layer to initiate coupling with the unreacted color-former material and to provide in the image-carrying layer a dye positive image which in this instance is magenta.

Imbibition time, namely, the time the exposed photosensitive layer 11 and the image-carrying layer 14 are kept in contact after the spreading of the liquid-processing solution, is for about 5 minutes, following which the image-carrying layer is separated from the photosensitive layer. This separation may be accomplished by stripping action, and any coating of film-forming material from the processing composition adhering to the image-carrying layer may be removed or allowed to remain thereon. Image formation while the photosensitive and image-carrying layers 11 and 14 are in contact is carried out in light to which the photosensitive layer is substantially insensitive and may be conveniently carried out by keeping the film unit in the dark by allowing it to remain in the camera apparatus employed to expose it until formation of the dye positive image has been completed. Of course, in instances wherein the outer layers of the film unit are opaque to actinic light, the unit may be removed from camera apparatus after the liquid-processing composition has been spread and image formation allowed to proceed under ordinary lighting conditions.

Example 2

A sheet 11-12 comprising a gelatino silver iodobromide emulsion on paper is dipped for two minutes in a bath containing .3 gram p-nitrophenylacetonitrile per 100 cc. of a mixture of 40 cc. acetone and 60 cc. of water, squeegeed, dried, rinsed with a solution comprising 90% acetone and 10% water and again squeegeed and dried after which it is ready for use.

An image-carrying layer for use with the above negative material is prepared by swabbing a sheet of baryta paper with a saturated solution of sodium perborate.

The modification of the invention described in Example 2, when exposed and processed in the previously described manner, gives a some-

what denser positive magenta image than that obtained in Example 1. Imbibition time in this example is for 5 minutes.

Example 3

In another embodiment wherein aerial oxidation is utilized, a photographic element is employed comprising a paper base 12 on which is coated a layer 11 of a commercial gelatino silver iodobromide emulsion similar to that employed with film sold by Eastman Kodak Company under the name of "Verichrome" film. As in all the examples contained herein, a color former may be incorporated in such emulsion prior to casting or by imbibition into the cast emulsion. Introduction of the coupler is accomplished by immersing a sheet 11-12 of the just-described character for two minutes in a bath containing 0.3 gram of p-nitrophenylacetonitrile per 100 cc. of a mixture of 40 cc. acetone and 60 cc. of water. Upon removal from the just-mentioned bath, the photosensitive layer 11-12 is dried in air and rinsed as by immersion for two seconds in a solution comprising 95% acetone and 5% water and quickly wiped to remove excess acetone solution. When dried, the treated sheet 11-12 is ready for use.

An image-carrying layer in this example is provided by dye-transfer paper which comprises a paper base or support having coated thereon a layer of gelatin which contains a mordant therein. A paper of this character intended for use in the present example is that sold by Eastman Kodak Company under the name of "Dye Transfer Double Weight F" paper.

A viscous alkaline aqueous solution of a secondary color-forming developing agent like that of Example 1 is employed as the liquid-processing composition in this embodiment of the invention.

The photosensitive layer of the film unit of this example may be exposed as already described and when processed with the image-carrying layer in the manner previously set forth will provide a magenta dye image in the image-carrying layer. Imbibition time is for about 5 minutes and may be carried out in the dark following which the image-carrying layer is separated from the photosensitive layer.

Example 4

In still another specific method of practicing the invention, a negative sheet material 11-12 is prepared as in Example 3 except that rinsing is carried out in acetone rather than in an acetone-water solution.

An image-carrying layer is prepared by swabbing the gelatin surface of imbibition paper, i. e., a paper base coated with gelatin, with a mixture made by adding 0.25 gram of cupric sulfate to 100 cc. of water. The paper is then swabbed with a 1% aqueous solution of potassium thiocyanate, washed for 5 minutes in running water, and dried. It is believed that the resulting paper contains cupric hydroxide and some copper thiocyanate.

For use with the just-described film unit, there is preferably provided a liquid composition prepared by mixing the following materials:

- 30 grams of a 6% water solution of medium viscosity sodium carboxymethyl cellulose
- 5 grams of sodium carbonate
- .2 gram 2-amino-5-diethylaminotoluene monohydrochloride
- 10 cc. of water

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A contrasty positive magenta image is obtained when the film unit is exposed and processed in accordance with practices already set forth. Imbibition time is about 5 minutes.

Example 5

In still another embodiment, a negative material like that of Example 3 is prepared as in that example but is treated with only 0.1 gram of p-nitrophenylacetonitrile per 100 cc. of 40% acetone. After treatment in this solution for 2 minutes, the negative material is removed and dried.

An image-carrying layer is provided by imbibition paper swabbed as in Example 4 and a liquid-processing composition like that of Example 4 is employed.

It is to be observed that in this example rinsing of the negative sheet material in acetone is omitted as it has been found that such practice is unnecessary when the image-carrying layer has a copper compound therein.

When the film unit of this example is exposed and processed as previously described, a magenta positive image of relatively high maximum density is obtained. Imbibition time is about 5 minutes.

Example 6

To obtain a cyan positive image, a photosensitive layer 11 comprising a relatively "fast" orthochromatic silver iodobromide gelatin emulsion on paper 12 is immersed for 2 minutes in a bath containing 0.3 gram of 2,4-dichloro-1-naphthol per 100 cc. of a solution which comprises 40% acetone and 60% water. The negative material is squeezed and after drying is ready for use.

A sheet of imbibition paper is prepared as an image-carrying layer by swabbing the gelatin face thereof with a solution made by adding 0.25 gram of cupric sulfate per 100 cc. of water.

When the film unit of Example 6 is exposed and processed in the manner heretofore described, making use of the developing agent of Example 4, a cyan positive image is provided in the image-carrying layer. Imbibition time is about 7 minutes.

Example 7

The whiteness of the highlights of the positive image may be improved in the preceding examples by incorporating a preservative for the developing agent, in addition to the oxidizing agent, in or on the surface of the image-carrying layer. A preservative such as formaldehyde sodium sulfoxylate, sold by General Dyestuff Corp. under the name of "Rongalite C" is effective in reducing staining of the highlights in the positive image caused by oxidized developing agent. The preservative functions to delay action of the oxidizing agent until the liquid-processing composition has penetrated into the photosensitive layer where developing agent which could stain highlights in the positive image becomes exhausted. This action of the preservative appears to be effected without serious reduction of speed of development of the negative or density of the dye positive image.

As a specific illustration, an image-carrying layer for a film unit such as that in Fig. 1 is provided by imbibition paper which is treated with cupric sulfate as in Example 6 and is then swabbed with a 1% aqueous solution of "Rongalite C" (formaldehyde sodium sulfoxylate). Excess "Rongalite C" is removed and the layer is dried.

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A cyan positive image having good clarity of highlights is obtained when the just-described image-carrying layer is used in a film unit employing the photosensitive layer of Example 6 and the liquid-processing composition of Example 4, exposure and processing being similar to the practices previously noted. In this example the film unit is maintained in assembled condition for about 7 minutes after spreading of the liquid composition.

Example 8

Another example for providing a cyan positive image makes use of a negative material like that of Example 6, namely, a relatively "fast" orthochromatic iodobromide emulsion on a paper base. The color former is incorporated in the photosensitive layer by treatment of the photosensitive layer for one minute in a bath containing 0.3 gram of 2,4-dichloro-1-naphthol per 100 cc. of a solution comprising 60% acetone and 40% water. Excess coupler solution is removed from the negative material, which upon drying is ready for use.

The image-carrying layer in this example is provided by imbibition (gelatin coated) paper, the gelatin surface of which has been swabbed with a solution comprising 0.5 gram of cupric sulfate per 200 cc. of water, and dried.

A liquid-processing composition in this example comprises a mixture of the following materials:

7.2 grams sodium carboxymethyl cellulose (medium viscosity)
150 cc. water
20 grams sodium carbonate (monohydrated)
0.8 gram 2-amino-5-diethyl-aminotoluene monohydrochloride

Exposure and processing of the film unit of this example are in the manner previously described. With an imbibition time of 5 minutes, a satisfactory cyan positive image is obtained in the image-carrying layer.

Example 9

A yellow positive image is obtained by the similar processing of a film unit like that of Example 8 except that a coupler capable of forming a yellow dye is employed. In this instance, the photosensitive layer has the coupler incorporated therein by immersion for 1 minute in a solution comprising 0.3 gram of acetoacet-2-chloroanilide per 100 cc. of a solution comprising 40% acetone and 60% water.

Example 10

Positive images comprising a dye of a color other than magenta or cyan or yellow may also be obtained by appropriate practice of the invention. Thus, a rose-colored positive image may be formed by the similar processing of a film unit like that described in Example 8 but with the use of a coupler capable of forming a rose-colored dye when reacted with the developing agent of that example. In this instance the photosensitive layer has the coupler incorporated therein by immersion for one minute in a bath comprising 0.3 gram of 1-phenyl-3-methyl-5-pyrazolone per 100 cc. of a solution comprising 40% acetone and 60% water.

Example 11

An orange-red dye positive image may be provided with the use of negative material like that of Example 8 but which is treated for one minute in a bath containing 0.1 gram of p-nitrophenyl-

acetonitrile per 100 cc. of a solution comprising 40% acetone and 60% water, squeegeed and dried.

Like Example 8, imbibition paper treated with cupric sulfate solution is employed to provide the image-carrying layer. However, in this embodiment a mixture of the following materials is employed for the liquid-processing composition:

1.5 grams sodium carboxymethyl cellulose (medium viscosity)
33.5 cc. water
5.0 grams sodium carbonate
0.2 gram 2,5-diaminotoluene sulfate

The film unit of this example is adapted to be subjected to exposure and processing in the manner already set forth, imbibition time of about 5 minutes being employed.

Example 12

As previously pointed out, dye positive images of a color other than those heretofore mentioned are obtainable when several couplers are employed in the photosensitive layer rather than a single coupler. The result of such expedient is to give a positive image having a color different from each of the individual dyes formed during processing. Thus, it is possible to form black and white dye positive images by the color forming of appropriate dyes which, when added together, give a black. The attributes of any color obtained in this manner is of course dependent upon the specific color formers employed and their proportions in the mixture.

This embodiment of the invention may be specifically illustrated with reference to a bluish-gray and white positive. For this purpose, a photographic element is provided through the use of a relatively "fast" orthochromatic iodobromide emulsion on a paper base such as that noted in Example 8. A coupler mixture is incorporated in this negative material by the immersion thereof for one minute in a solution containing .12 gram p-nitrophenylacetone, .6 gram 2,4-dichloro-1-naphthol and .6 gram acetoacet-2-chloroanilide per 80 cc. of water. The usual squeegeeing and drying steps follow this immersion of the negative material in the coupler solution.

An image-carrying layer suitable for use with the just-described photosensitive layer assembly is prepared by swabbing the gelatin surface of imbibition paper with a mixture made by adding .25 gram of cupric sulfate to 100 cc. of water, following which the paper is swabbed with a 5% aqueous solution of potassium thiocyanate, washed for 5 minutes in running water and dried.

In this embodiment, a liquid-processing composition is employed which comprises:

145 grams of a 5% water solution of medium viscosity sodium carboxymethyl cellulose
10 grams of sodium carbonate (monohydrated)
.4 gram of 2-amino-5-diethylaminotoluene monohydrochloride
15 cc. of water

Exposure and processing practices are like those already set forth, the film unit being maintained in assembled condition for about 5 minutes, after which the image-carrying layer is suitably separated, and is found to carry a positive dye image of good quality having a bluish-gray and white color.

Example 13

The desirability of incorporating the developing agent in the photosensitive or negative layer of

a film unit has been pointed out as of value in effecting complete development of the areas of the negative in which exposure has occurred whereby to exhaust the developing agent in such areas and prevent its migration therefrom into contact with the image-carrying layer as well as being of value in reducing stain in the image-carrying layer by premature oxidation of the developing agent before it has reacted with exposed silver halide in the negative.

One practice for carrying out this embodiment may be illustrated with a film unit 10 having negative material like that already referred to as comprising a relatively "fast" orthochromatic iodobromide emulsion on a paper support. The developing agent and color former are incorporated in such negative by immersing the same for 1½ minutes in a bath containing 0.05 gram of 2-amino-5-diethylaminotoluene monohydrochloride and 0.1 gram of p-nitrophenylacetone per 100 cc. of a solution comprising 40% acetone and 60% water. The pH value of the photosensitive layer prepared in this manner is sufficiently low to retard aerial oxidation of the developing agent carried in the layer.

An image-carrying layer for use in this example is prepared by swabbing imbibition paper with a solution of cupric sulfate and then with a solution of potassium thiocyanate in the manner and in the proportions set forth in Example 4.

In this instance, the liquid-processing composition contains no developing agent and comprises a solution of the following materials in the proportions noted:

5 grams sodium carboxymethyl cellulose
16 grams sodium carbonate (monohydrated)
100 cc. water

Exposure and processing is in the manner described with imbibition time of about 5 minutes and results in a positive magenta image quite free from stain in the highlights.

Example 14

In another illustration, the coupler and developing agent are incorporated in the photosensitive layer of negative material like that of Example 13 in the following manner. The negative material is immersed for 1 minute in a bath containing 0.2 gram of p-nitrophenylacetone per 100 cc. of a solution of 50% acetone and 50% water. Excess coupler solution is removed from the negative material which is dried and immersed in a bath containing 0.5 gram of 2-amino-5-diethylaminotoluene monohydrochloride per 100 cc. of water, following which excess developing agent is removed as by squeegeeing the negative material which upon drying is ready for use. Loss of emulsion speed is greatly reduced by incorporating the color former and developing agent in the emulsion from separate solutions rather than by the practice of Example 13.

An image-carrying layer is imbibition paper, prepared by swabbing the gelatin surface thereof with a solution containing 0.25 gram of cupric sulfate per 100 cc. of water.

In this instance, the processing composition comprises a solution of the following materials in the proportions given:

5 grams sodium carboxymethyl cellulose
10 grams sodium carbonate
100 cc. water

Exposure and processing in the usual manner with imbibition time of about 5 minutes gives a

magenta positive image of good quality, and free of developer stain.

Example 15

When the developing agent is incorporated in some layer other than the emulsion layer, a unit may be employed which utilizes a negative material 21—22 comprising a paper-based relatively "fast" orthochromatic iodobromide emulsion of the character noted earlier herein, the unit also including a layer 27 in which the developing agent is distributed. Prior to formation of layer 27, element 21—22 is imbibed for one minute in a bath which contains color-former material and which comprises 0.2 gram of p-nitrophenylacetonitrile per 100 cc. of equal parts of acetone and water.

After squeegeeing and drying, element 21—22 is coated with a layer of material containing a developing agent. This material should be of a film-forming character and also should be enteric, i. e., soluble in organic solvents and alkali but insoluble in water whereby to minimize penetration of the developing agent into the emulsion prior to processing. One suitable enteric and film-forming material is cellulose acetate hydrogen phthalate which with a developing agent is mixed in a mutual solvent to provide a composition of the following proportions:

2 grams 2-amino-5-diethylaminotoluene monohydrochloride
2 grams cellulose acetate hydrogen phthalate
100 cc. methyl Cellosolve (2-methoxy ethanol)

This composition is coated onto photosensitive layer 21 of unit 20 by conventional practice, for example, it may be doctored or roll-coated thereon. This coating completes the negative material, which upon drying is ready for use. Placement of the developing agent in some layer of the unit other than the emulsion advantageously avoids loss in emulsion speed while making the developing agent available to the negative material before it becomes available to the image-carrying layer during processing.

An image-carrying layer in this example is imbibition paper swabbed with a 1% water solution of cupric sulfate.

The liquid-processing composition in this example comprises a mixture of the following materials in the proportions noted:

5 grams sodium carboxymethyl cellulose
16 grams sodium carbonate (monohydrated)
100 cc. water

Exposure and processing of the film unit 20 is in the usual manner already described and results in the formation of a magenta positive image in the image-carrying layer. Imbibition time is for 5 minutes.

Example 16

The following example may be used to illustrate the use of a film unit such as that shown in Fig. 3 wherein the developing agent is carried in a layer 37 between the emulsion base 32 and the emulsion 31 of the photosensitive layer. One manner of forming such a film unit is to cast or coat the emulsion base with a layer-forming material containing the developing agent and then to apply the emulsion onto the coated layer. This may be accomplished by employing baryta paper for the base 32 and coating one face thereof with the solution of the developing agent in cellulose acetate hydrogen phthalate of Example 15

whereby to provide layer 37 on the base 32. A silver halide emulsion having a coupler incorporated therein may then be cast on the layer containing the developing agent, or the emulsion of a conventional film or paper may be transferred onto the layer 37.

As illustrative of the latter expedient, a paper-based relatively "fast" silver iodobromide emulsion in unhardened condition is softened in warm water and peeled from its base to permit it to be bodily transferred onto the layer 37 containing the developing agent. When the transferred emulsion of this character is without a coupler, a suitable color former may be incorporated therein by swabbing it with a mixture containing 1 gram of p-nitrophenylacetonitrile per 100 cc. of a solution comprising 80% acetone and 20% water. The negative material is then squeegeed and upon drying, is ready for use.

An image-carrying layer for use in this illustration is imbibition paper prepared by bathing it for one minute in a solution comprising 0.25 gram of cupric sulfate per 100 cc. of water and is then dried whereupon it is ready for use.

A liquid-processing composition for use with this example of the invention is that given in Example 15.

Exposure and processing of the film unit of Fig. 3, prepared as noted in Example 16, is carried out in the usual manner with an imbibition time of about 5 minutes. This practice produces a magenta dye positive image.

The aerial oxidation disclosed in Fig. 3 is applicable in all other illustrative examples of the invention, whereby it is possible to omit an oxidizing agent from the image-carrying layer and to create a dye image therein by permitting air to effect oxidation of the unreacted developing agent in the imagewise distribution of the unreacted developing agent and the unreacted color-forming material. Processing in this manner is comprehended by the invention, although the use of an oxidizing agent is preferred as it speeds up the oxidation reaction and thereby increases the density of the positive image.

Likewise, while a liquid container, such as the container 16, provides a convenient means for spreading a liquid composition between layers of a film unit whereby to permit the processing to be carried out within a camera apparatus, the practices of this invention may be otherwise effected. For example, a photosensitive layer after exposure in suitable apparatus and while preventing further exposure thereof to actinic light may be removed from such apparatus and permeated with the liquid-processing composition as by coating the composition on the photosensitive layer or otherwise wetting the layer with the composition, following which the permeated layer, still without exposure to actinic light, is brought into contact with an image-carrying layer for image formation in the manner heretofore described.

Throughout the specification reference has been made to the use of developing agents of the character known as secondary color-forming developing agents. While secondary color-forming developing agents are preferred, it will be realized that a primary color-forming developing agent may also be employed. A primary color-forming developing agent is a developing agent which couples with itself to form a dye and as examples thereof suitable for use in the practice of the invention mention may be made of 1,5-dihydroxy-naphthalene; 4-chloro-2-

methyl-aminophenol; and 4-amino-5-pyrazolone.

For the purpose of simplicity, the invention has been illustrated and described in connection with a film unit of the roll film type. The invention, however, is not limited to this type of film and may be employed with cut film in a film pack type of unit. An example of this latter embodiment, useful for carrying out the practices of the present invention, forms the subject matter of application Serial No. 707,966, filed November 5, 1946, by Edwin H. Land, for Photographic Product, now Patent 2,495,111.

Throughout the specification and appended claims the expression "positive image" has been used. This expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive layer. As an example of an alternative meaning for "positive image," assume that the photosensitive layer is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive layer will be a positive and the image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the color black.

Throughout the specification and claims the expression "superposing" has been employed. This expression is intended to cover the causing of one layer to become attached or united in a permeable relationship with another layer, in the manner of a stratum. While a face-to-face contact is a preferred form of superposition, the expression "superposing" is intended to be generic to a relationship wherein there exists a third layer in the stratum between the two layers, such for example as shown in Fig. 2, or where a layer of a viscous liquid exists between the superposed layers.

As previously pointed out, while a high viscosity for the liquid processing composition is desirable to assist in its spreading, the invention may be successfully practiced without the use of a film-forming material in the composition. As illustrative of this latter expedient, reference is made to the processing compositions of the preceding examples, all of which are employable for processing purposes by the substitution of water for the sodium carboxymethyl cellulose in a quantity equivalent to such film-forming material. In instances when containers are not employed, a nonviscous processing composition is particularly applicable and may be applied to the negative material by imbibition or coating practices and may be similarly applied to the image-carrying layer before the latter and the negative material are brought into contact.

The invention finds particular utility in the field of color photography and, in addition to providing for the formation of monochromatic or images of a single color, is useful in providing multicolor images. In the latter regard, two or more image-carrying layers, each containing an individual color component image of a multicolor image, may be assembled in superposed and registered relation on a common base in a manner well understood by the art whereby to provide the desired multicolor image.

Likewise, the inventive concepts herein set forth are adaptable for multicolor work carried out with special film units wherein two or more appropriately sensitized layers are associated with a like number of image-carrying layers in the manner of the film units disclosed in application Serial No. 730,661, filed February 25, 1947, by Edwin H. Land for Photographic Product and Process. In lieu of this practice tripack film prepared with coupler and/or developing agent in the manner herein set forth may be employed as negative material, and after exposure each layer thereof may be developed and treated in accordance with the preceding disclosures in conjunction with individual image-carrying layers.

Also included within the scope of the present invention is the formation of a plurality of dye component images in the same image-carrying layer by successively bringing the image-carrying layer into registered contact with individual negative elements, each of which latter contains a negative latent image representative of a positive color component image to be formed in the image-carrying layer. In such practice, the image-carrying layer may, if desired, be treated with a solution of an oxidizing agent during the course of processing and intermediate the formation of a successive pair of positive color component images.

Furthermore, the invention is useful for copying purposes from separation positives with any of the types of film units described. Of course when the invention is used in the production of photographic originals, the spectral sensitivity of the different emulsion layers must be suitably chosen. For instance, instead of using an orthochromatic emulsion, a panchromatic or a specially red sensitized emulsion is employed for producing a cyan positive image. However, for copy work from separation positives, this is obviously unnecessary.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of forming positive images in color which comprises, developing a latent negative image in a silver halide emulsion layer of a photosensitive element with a color-forming developing agent dissolved in an aqueous alkaline liquid which is absorbed into said photosensitive element and is uniformly distributed throughout said emulsion layer and dissolving coupler material, reactable with oxidized developing agent to form image dye, in liquid which has been absorbed into said photosensitive element after said absorption has occurred whereby to effect the formation of a dye image in situ with a silver image developed by developing agent distributed in said emulsion layer while providing in said emulsion layer an imagewise distribution of unreacted developing agent and unreacted coupler material; transferring from said emulsion layer by imbibition at least part of said imagewise distribution of unreacted developing agent and unreacted coupler material to an image-carrying layer superposed with said photosensitive element in such close proximity thereto as to receive a depthwise diffusion of liquid from said emulsion layer without appreciably disturbing the image-

wise distribution of components contained in said liquid; and oxidizing said transferred developing agent in said image-carrying layer and reacting the oxidized product with said unreacted coupler material in said image-carrying layer to form a dye whereby to provide a positive image of said latent image.

2. The process of forming positive images in color as defined in claim 1 wherein the image-carrying layer and the photosensitive element are separated from superposed relationship at some stage of said process after the imagewise distribution of unreacted developing agent and unreacted coupler material has been transferred from the emulsion layer of said photosensitive element to said image-carrying layer.

3. The process of forming positive images in color which comprises, spreading an aqueous alkaline liquid in a layer between and in contact with a photosensitive element comprising a silver halide emulsion layer having a latent negative image therein and a sheet material comprising at least an image-carrying layer, absorbing said liquid into said photosensitive element including said emulsion layer, developing said latent image with a color-forming developing agent which is dissolved in said liquid and introducing a coupler material, which is reactable with oxidized developing agent to form dye and which is dissolvable in said liquid substantially only in liquid present in said photosensitive element as a result of said absorption whereby to develop said latent image to silver and to form a dye image in situ therewith and as a result of said development providing an imagewise distribution of unreacted developing agent and unreacted coupler material in said emulsion layer, transferring from said emulsion layer by imbibition at least part of said imagewise distribution of unreacted developing agent and unreacted coupler material to said image-carrying layer to provide in the image-carrying layer a depthwise diffusion of liquid from said emulsion layer without appreciably disturbing the imagewise distribution of components contained in said liquid, and oxidizing said transferred developing agent and reacting it with transferred coupler material in said image-carrying layer to form a dye whereby to provide a positive image of said latent image.

4. The process of forming positive images in color as defined in claim 3 wherein the image-carrying layer and the photosensitive element are separated from superposed relationship at some stage of said process after the imagewise distribution of unreacted developing agent and unreacted coupler material has been transferred from the emulsion layer of said photosensitive element to said image-carrying layer.

5. The process of forming positive images in color which comprises, absorbing an aqueous alkaline liquid into a photosensitive element having a silver halide emulsion layer containing a latent image, said liquid comprising a solvent for a color-forming developing agent and coupler material, said absorbed liquid being permeated into said emulsion layer, dissolving a color-forming developing agent and coupler material reactable with oxidized developing agent in liquid contained in said photosensitive element substantially only by said absorption whereby to uniformly distribute unreacted developing agent and unreacted coupler throughout said emulsion layer and thereby cause the development of said latent image to silver and the formation of a dye image in situ therewith while forming in said

emulsion layer an imagewise distribution of unreacted developing agent and unreacted coupler material, transferring from said emulsion layer by imbibition at least part of said imagewise distribution of unreacted developing agent and unreacted coupler material to an image-carrying layer superposed with said photosensitive element in such close proximity thereto as to receive a depthwise diffusion of liquid from said emulsion layer without appreciably disturbing the imagewise distribution of components contained in said liquid; and oxidizing said transferred developing agent in said image-carrying layer and reacting the oxidized product with said unreacted coupler material in said image-carrying layer to form a dye whereby to provide a positive image of said latent image.

6. The process of forming positive images in color which comprises, spreading in a layer between and in contact with a photosensitive element comprising a silver halide emulsion layer having a latent negative image therein and a sheet material comprising at least an image-carrying layer, an aqueous alkaline liquid which is a solvent for color-forming developing agent and coupler material reactable with oxidized developing agent to form dye but from which developing agent and coupler material are absent; absorbing said liquid into said photosensitive element including said emulsion layer; dissolving a developing agent and a coupler material reactable with oxidized developing agent to form dye in liquid present by absorption in said photosensitive element whereby to develop said latent image to silver and form a dye image in situ therewith and as a result of said development providing an imagewise distribution of unreacted developing agent and unreacted coupler material in said emulsion layer, transferring from said emulsion layer by imbibition at least part of said imagewise distribution of unreacted developing agent and unreacted coupler material to said image-carrying layer to provide in the image-carrying layer a depthwise diffusion of liquid from said emulsion layer without appreciably disturbing the imagewise distribution of components contained in said liquid; and oxidizing said transferred developing agent and reacting it with transferred coupler material in said image-carrying layer to form a dye whereby to provide a positive image of said latent image.

7. In a photographic product of the character wherein a photosensitive element, having at least one layer which comprises a silver halide emulsion layer, is associated with a base layer for receiving a transfer image and a container holding at least an aqueous alkaline liquid solvent for a photographic developer, and wherein said photosensitive element, said base layer and said container are held together to permit at least a portion of said base layer and said photosensitive element to be superposed with said container so positioned as to be capable of being ruptured and without removal of its ruptured portion of releasing its liquid content between two layers of said product to at least partially permeate the superposed base layer and photosensitive element including said silver halide emulsion layer, in combination, a silver halide developer positioned within said product, said developer being characterized by the fact that the oxidation product thereof is reactable with coupler material to form image dye and that said developer is soluble in said liquid, the release of said liquid rendering said developer effective to develop a

latent image in said emulsion layer and the result of development of the emulsion layer being the formation therein of a differential disposition of unreacted developing agent which is adapted to be transferred to said base layer for effecting the formation of a reversed dye image of the subject matter of said latent image, and coupler material, which is reactable with oxidized developer for effecting dye formation and which is soluble in said liquid, distributed throughout a layer of said photosensitive element, said layer containing coupler material being located in said photosensitive element at least in a position for contact of said coupler material with liquid adapted to be transferred to said base layer and containing unreacted developer in solution.

8. A photographic product as defined in claim 7 wherein an oxidizing agent which is substantially inactive with respect to image dye is substantially uniformly distributed at least throughout a stratum of said base layer.

9. A photographic product as defined in claim 7 wherein said photosensitive element in addition to said silver halide emulsion layer comprises another layer formed of a permeable material and wherein said developer is substantially uniformly distributed within one of said just named layers and said coupler material is substantially uniformly distributed within the other of said just named layers.

10. A photographic product as defined in claim 7 having a photosensitive element comprising, in addition to said silver halide emulsion layer, a layer of a permeable material superposed with

respect to said emulsion layer, and having said developer contained in one of said just named layers and a coupler material contained in the other of said just named layers, and wherein an oxidizing agent which is substantially inactive with respect to image dye is contained within said base layer for contact with liquid transferred to the base layer and containing unreacted developer and unreacted coupler material in solution.

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